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Effect of supercritical extraction on the soot nanostructure and gasification product yields

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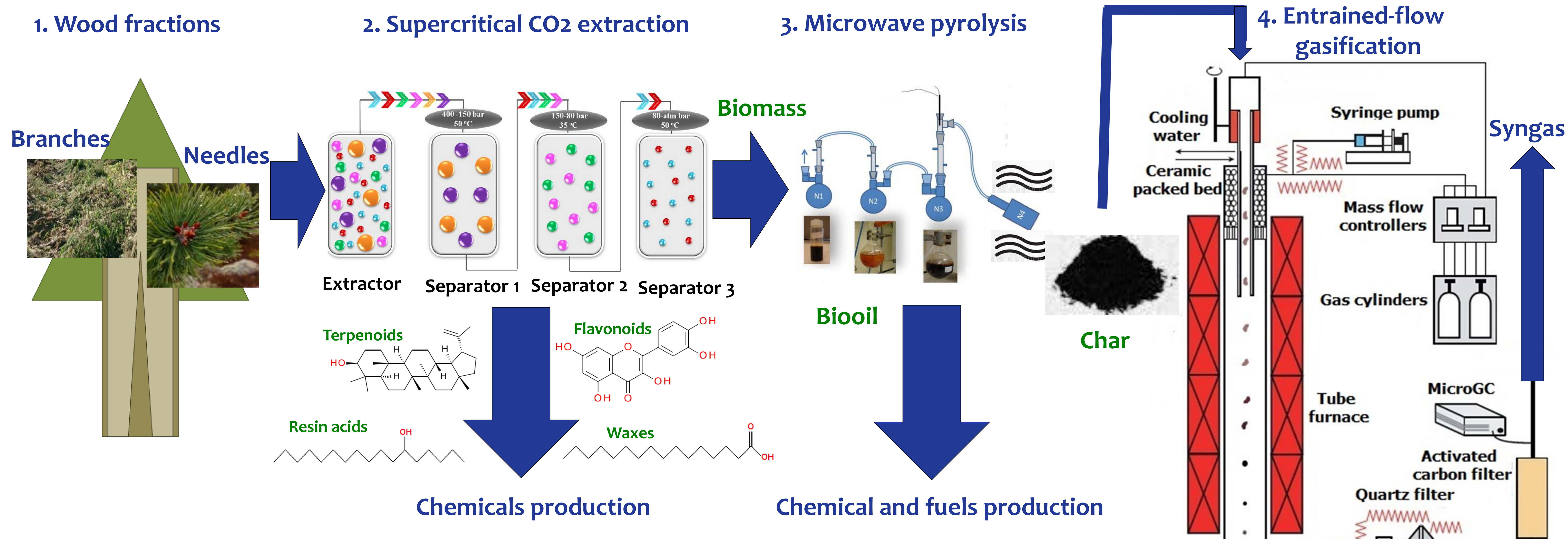
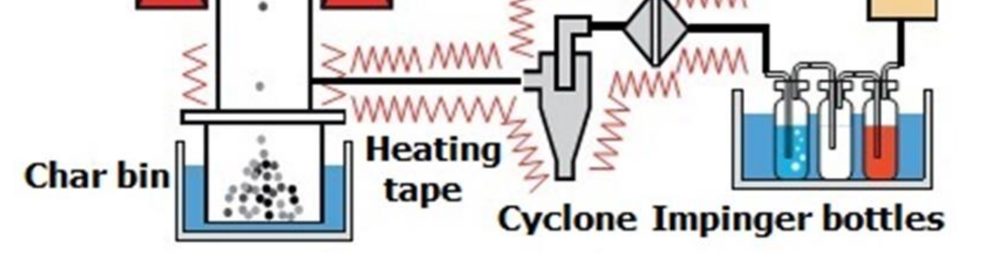
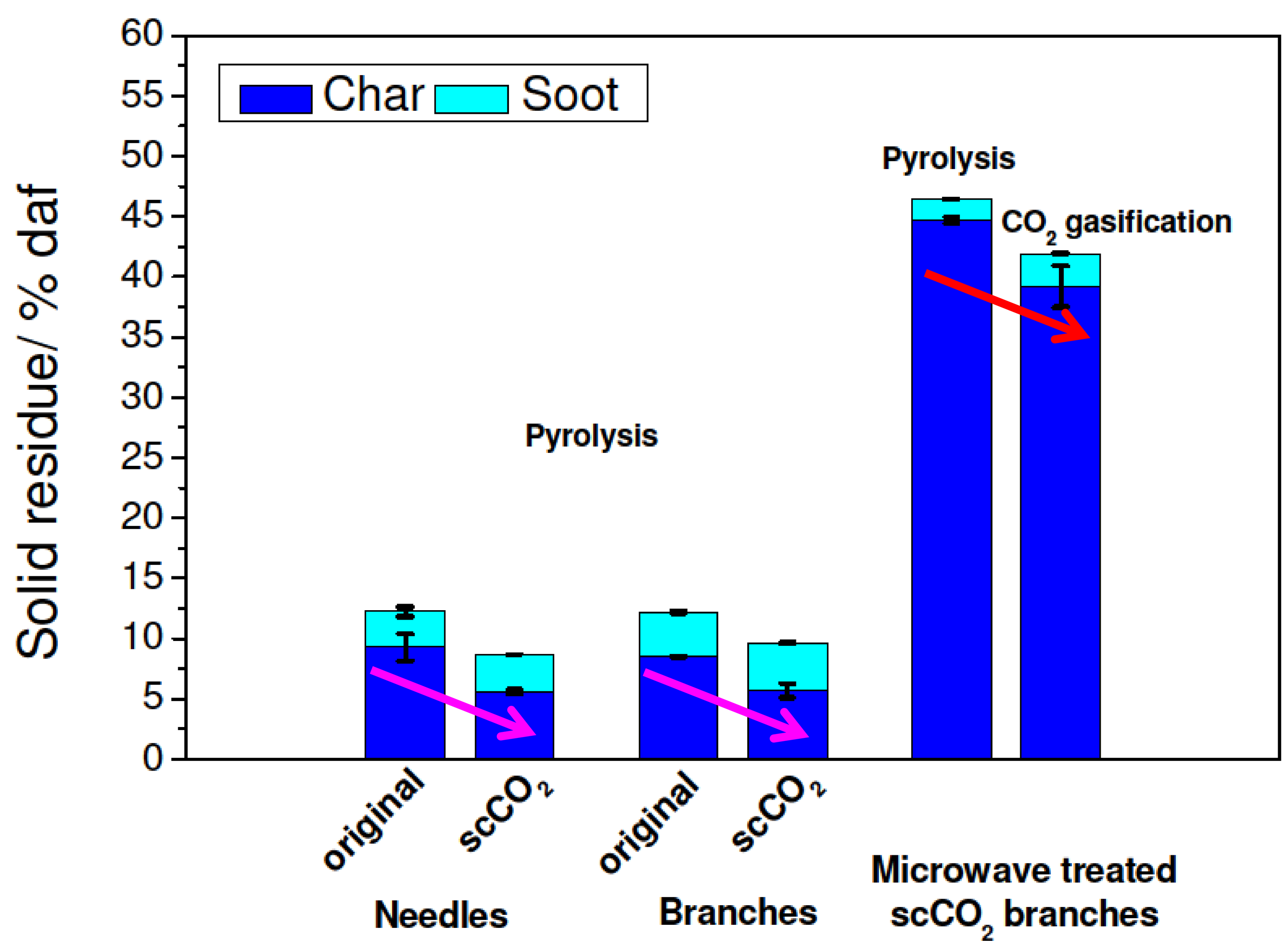
Introduction: The cost-efficient development of biorefinery depends on feedstock flexibility and combination of pre-treatment processes with the power and heat generation [1]. The pre-treatment processes decrease the water content in feedstock, increase energy density, and bring the high value-added products to the chemical and liquid fuel industries, whereas the remaining solid fuel fractions are used for the renewable and clean energy generation. Supercritical carbon dioxide extraction significantly reduces the risks associated with off-gassing and oxygen depletion during fuel storage [2], while the extracted fatty acids can be utilized as a primary feedstock for chemicals and biorefinery applications [3,4]. In addition, the high content of extractives in softwood might create challenges with fuel feeding and conversion during gasification. Forest industry produces millions of tons of waste wood residues which can be used in a closed loop efficient process. The supercritical extraction and biomass microwave pyrolysis have a high potential to remove extractives and other volatile compounds, and thus, to reduce the formation of solid residues in the entrained flow gasification.

Closed loop biorefinery process

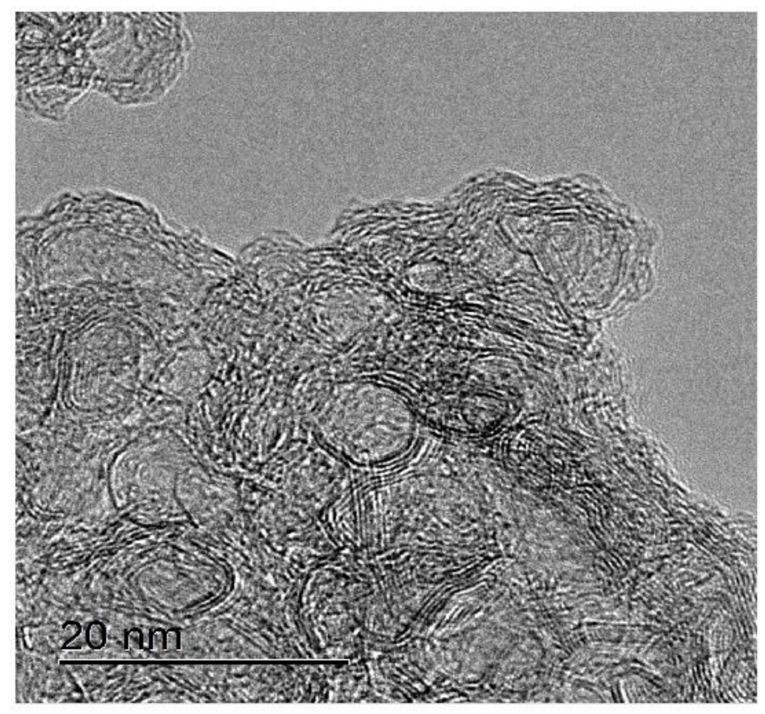




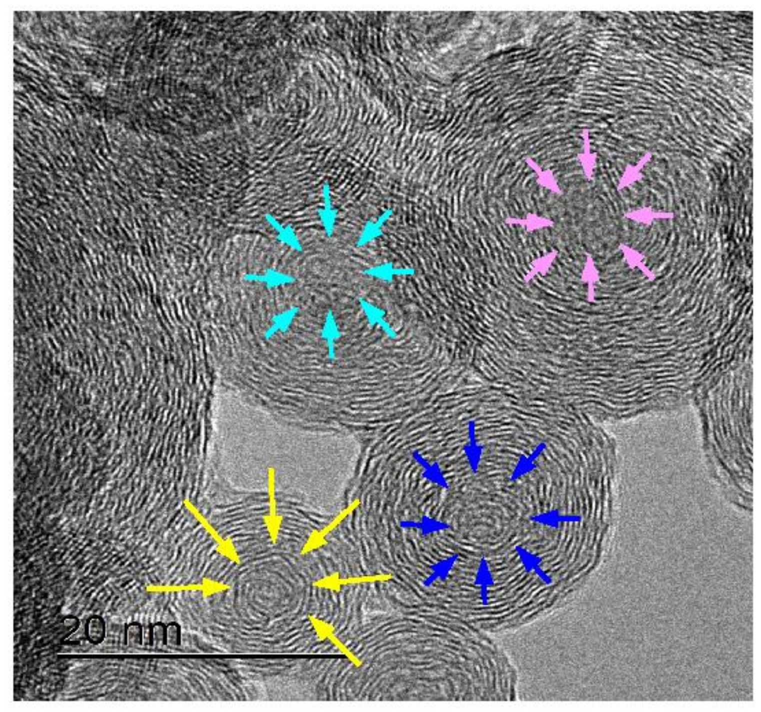
Methodology: Original and supercritical CO2 extracted needles and branches were pyrolyzed at 1100°C in the drop tube reactor (DTF). The results were compared with $scCO_2$ extracted branches which were firstly treated in a microwave reactor and subsequently reacted in the DFT under pyrolysis and CO_2 gasification conditions.



Soot from original needles



Soot from scCO2 extracted needles



Conclusion and Future studies: The results showed that biomass pre-treatment using supercritical CO_2 extraction is a promising way to decrease char yield in high temperature processes with the concomitant production of an added-value feedstock in the green chemical and energy industry. Optimized supercritical extraction conditions allowed to extract more than half of fatty and resin acid compounds from pine needles and branches. Supercritical extraction had no influence on the soot yield, whereas the differences in nanostructure of soot from original needles and branches and samples after $scCO_2$ were obvious. Soot particles from original wood fraction were irregular-shaped with the longer graphene segments (13.2 nm) and lower curvature compared to soot particles from $scCO_2$ extracted wood fractions which obtained a structure similar to soot from low ash-containing stemwood. The additional heat treatment of char from microwave pyrolysis led to the low soot yield and high syngas formation under pyrolysis and CO_2 gasification conditions. Microwave pyrolysis of scCO2 treated branches has potential to produce liquid products for the chemicals and fuels, whereas the remaining char can be used as a feedstock in high temperature processes. Future studies are planned to scale up supercritical CO2 extraction, microwave pyrolysis and entrained flow gasification to the industrial pilot plant.

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